FRACTIONATION AND MOLECULAR ANALYSIS
OF A VACUUM RESIDUE ASPHALTENES

Ming-Gang Yang[1] and Semih Eser[1, 2]

1.Lab.for Hydrocarbon Proc.Chem, The Energy Institute, Penn State Univ., 209 Acad. Proj. Bldg.
2. Dept. of Energy and Geo-Environmental Eng., Penn State Univ., 154 Hosler Building,
University Park, PA 16802

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INTRODUCTION

Petroleum asphaltenes are defined as the n-pentane or n-heptane insoluble but toluene soluble fraction of crude oils or petroleum residua. This operational definition is a consequence of the extremely complex structure of asphaltenes which consist of thousands of compounds containing highly aromatic cores, long chain aliphatic groups, heteroatoms (sulfur, nitrogen, and oxygen) as well as trace quantities of heavy metals (vanadium and nickel). Therefore, it is extremely difficult to elucidate the molecular structure of petroleum asphaltenes.

A number of studies have been carried out including asphaltene pyrolysis[1, 2], chemical reduction[3] and oxidation (RICO)[4] with catalysts using many analytical techniques[5-9] such as GC-MS, MALDI, LDIMS, HRMS, ^{1}H/^{13}C NMR, FT-IR, UV-vis spectra, EXAFS, SEC, ESR, XRD, SANS, etc., to investigate the asphaltene structure at the molecular level. The results from these studies have brought to light a wealth of valuable information on asphaltenes. Recent structural models suggest that asphaltene molecules be composed of an aromatic core with six condensed aromatic rings on average that is substituted by n-alkyl groups averaging C_8 in length[10]. In addition, bridging polymethylene groups may be present which connect the aromatic core to smaller aromatic and thiophenic rings. In general, about 25% of the sulfur is thermally labile alkyl and cyclic sulfides, while the remaining sulfur is present in the aromatic core along with the majority of the N and O heteroatoms [11, 12]. The distribution and structure of the heteroatoms in the aromatic core is largely unknown. The molecular weight of individual asphaltene molecules averages less than 1000 amu, but the asphaltene molecules interact strongly in solution, forming colloidal aggregates with very high apparent molecular weights[13].

In this study, a petroleum residue asphaltenes were separated into six subfractions based on their solubility in binary solutions of n-pentane and toluene at different proportions. The separated subfractions were analyzed by laser desorption ionization mass spectrometry (LDIMS), ^{1}H/^{13}C NMR, and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS).

EXPERIMENTAL

The n-pentane (HPLC grade, 99.8 %) and toluene (HPLC grade, 100 %) were supplied by Fisher Chemicals, and J.T. Baker Inc. respectively. Chloroform-d (99.8 atom% D) and Chrom(III)-acetylacetonate (97 % UV) used in ^{1}H/^{13}C NMR analysis were supplied by Aldrich Chemical Company, Inc., and Fluxa Chemika. A commercial petroleum vacuum residue sample was used as a source of asphaltenes.

The vacuum residue sample was separated into maltenes (n-pentane soluble) and asphaltenes (n-pentane insolubale) by adding n-pentane in a volume/weight ratio of n-pentane to residue of 60:1 (mL/g) followed by filtration. A sample of 1 g asphaltenes was dissolved in 27 mL toluene, and 33 mL n-pentane was added into the solution by stirring with a magnetic bar at ambient temperature. After adding n-pentane, the ratio of the total volume of the two solvents to asphaltenes was 60:1 mL/g with an n-pentane to toluene ratio of 55/45 in volume. The solution was covered and stirred overnight for precipitation of insolubles. After filtration, the insoluble fraction was collected and dried in an oven at 75 °C and 0.1MPa vacuum overnight to obtain the first subfraction (Sample AS6). The n-pentane and toluene in the filtrate were evaporated in a rotary evaporator to collect the remaining asphaltenes that were dried in an oven at 75 °C and 0.1MPa vacuum overnight. The dried sample was dissolved in toluene again, and following the procedure described above, sample AS5 was precipitated in a solution with an n-pentane to toluene ratio of 65/35 in volume. Similarly, samples AS4 (n-pentane to toluene = 75/25), AS3 (85/15) and AS2 (95/5) were precipitated in binary solutions with the increasing proportion of n-pentane. The last fraction, AS1, (dissolved in the solution of n-pentane to toluene = 95/5) was obtained by evaporating the solvents. The asphaltene fractionation scheme is shown in Figure 1.
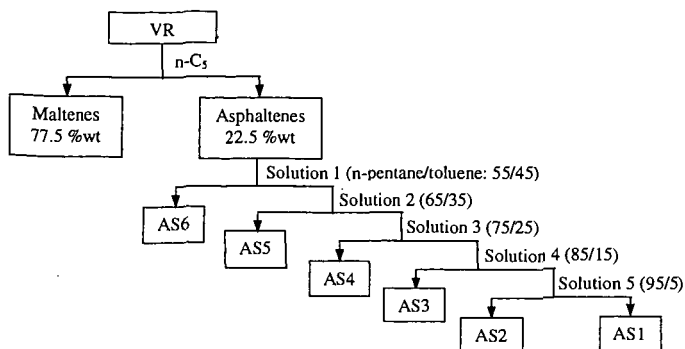
Figure 1. Flow chart for fractionation of petroleum vacuum residue asphaltenes.

The LDIMS spectra were acquired on a PerSeptive Biosystems Voyager-DE STR mass spectrometer using 337 nm light from a pulsed nitrogen laser for ionization. High-resolution spectra (M/ΔM ~ 10000 at m/z 500) were obtained using the reflector mode. Samples were prepared by dissolving approximately 50 micrograms of material in 200 microliters of tetrahydrofuran. The sample solution of 0.5 microliters was deposited on the gold-plated target, and the solvent allowed to evaporate under ambient laboratory conditions. Samples were introduced into the mass spectrometer and analyzed as soon as possible to minimize evaporation of more volatile components. Ionization was conducted using laser fluency slightly above the threshold for ionization (laser power ~ 106 W/cm^2), and a total of 256 laser shots acquired over numerous sites within each sample were averaged.

The NMR spectra were obtained using a BRUKER AMX360 NMR instrument operating at 360 MHz for ^{1}H NMR, and 89 MHz for ^{13}C NMR measurements. The NMR samples were prepared by dissolving about 100 mg asphaltenes into 1 mL chloroform-d solvent. Tetramethylsilane (TMS) was used as an internal standard mixed with chloroform-d solvent as received. A relaxation agent, chrom(III)-acetylacetonate, was added into the sample solution (0.03M) to get quantitative ^{13}C NMR measurements

For Pyrolysis-GC/MS experiments, samples (about 6 mg) were first loaded in an unsealed quartz tube. Then, the tube was inserted into a filament coil that is placed in the probe gun. The gun tube was inserted into an interface where the sample was pyrolyzed. Pyrolysis temperature, time, and the interface temperature were controlled by Pyroprobe 1000. Pyrolysis conditions were 800 °C, 10 seconds, and a heating rate of 5 °C/ms. The interface temperature was set 290 °C. Pyrolysis products were collected in a capillary column at liquid nitrogen temperature and then separated in a temperature programmed DB-17 capillary column by HEWLETT 5890 II GC, and characterized by HEWLETT 5971A MS.

RESULTS AND DISCUSSION

The petroleum vacuum residue contained 77.5 wt% maltenes and 22.5 wt% asphaltenes (n-pentane insoluble). Table 1 shows the yields of asphaltene subfractions separated following the scheme shown in Figure 1.

Table 1. Yields of solvent subfractions of asphaltenes.

Subfraction	AS1	AS2	AS3	AS4	AS5	AS6	Loss
Distribution / wt%	25.5	5.3	18.0	22.9	21.0	4.2	3.1

The results in Table 1 show that the vacuum residue asphaltenes could be further fractionated using the binary mixtures of n-pentane and toluene with different composition. The yields of subfractions AS2 and AS6 were much lower than those of the other subfractions.

Laser desorption ionization mass spectrometry (LDIMS) results in little fragmentation of the constituent molecules. Therefore, it is a useful technique to determine the molecular weight distribution in complex mixtures. The mass distributions of samples AS2, AS4 and AS6 are shown in Figure 2. Each asphaltene subfraction displayed a different molecular weight distribution. The distribution became wide and the number average molecular weight increased in mass/charge ratio from AS2 (250-600) to AS4 (300-800), and to AS6 (350-1100). The maximum abundance of

molecular constituents for the three samples, AS2, AS4, and AS6 is at 300, 350 and 500 m/z, respectively.

The ^{1}H NMR spectra have been divided into four regions consisting of γ-methyl hydrogens (H_γ) between 0 and 1 ppm; hydrogens from β-methyls, methines, and methylenes β or further to the aromatics (H_β) between 1 and 2 ppm; hydrogens from all aliphatic sites attached to aryl carbon (H_α) between 2 and 5 ppm; and aromatic hydrogens (H_{ar}) between 6 and 9 ppm. The ^{13}C NMR spectra have been divided into two integration domains which are aliphatic carbons (C_{al}) between 10 and 65 ppm, and aromatic carbons (C_{ar}) between 100 and 170 ppm. The hydrogen and carbon molar distributions derived from ^{1}H/^{13}C NMR spectra are listed in Table 2.

Table 2. Relative molar distribution of hydrogen and carbon in asphaltene subfractions

	AS2	AS3	AS4	AS5	AS6
H_α	0.17	0.33	0.12	0.21	0.37
H_β	0.63	0.43	0.62	0.57	0.49
H_γ	0.08	0.05	0.04	0.04	0.03
H_{ar}	0.12	0.19	0.22	0.18	0.11
C_{al}	0.60	0.54	0.53	0.52	0.51
C_{ar}	0.40	0.46	0.47	0.48	0.49

The carbon aromaticities of all the subfractions are similar to one another with a slightly lower aromaticity of AS2 compared to the other samples. There are, however, significant differences in the distribution of hydrogen between the subfractions. The relatively low hydrogen aromaticities of AS2 and AS6 can be attributed to more extensive alkyl substitution, and more condensed structures of aromatic ring systems, respectively. Differences in aliphatic hydrogen distribution between AS2 and AS6 also indicate variations in the nature of the alkyl groups. From the distribution of aliphatic hydrogen groups, similarities are noted between AS2 and AS4, and between AS3 and AS6. The fraction AS5 falls into an intermediate position between the two groups, particularly in H_α and H_β contents.

The average structural parameters do not give much information regarding the type and distribution of molecular constituents and their organization within the molecules. Pyrolysis GC/MS may provide some useful data on thermally labile molecular units and how they are connected. Asphaltenes during Py-GC/MS experiment were converted into three fractions: volatiles, nonvolatile heavy oils or tar, and remainder coke (tetrahydrofuran insoluble). The yield of each fraction was dependent on the pyrolysis conditions and the sample used. The sample AS2, for example, gave volatile fraction yield of 11.8 wt% at 600 °C, while at 800 °C, the yield increased to 45.2 wt%. The yields of volatile fractions from samples AS1 to 6 at 800 °C are listed in Table 3. The samples AS1 and AS6 showed higher yields of volatile fraction than samples AS3 and AS5.

Table 3. Yields of volatile fraction in asphaltene pyrolysis at 800 °C.

Sample	AS1	AS2	AS3	AS4	AS5	AS6
Yield / wt%	54.7	45.2	33.1	41.5	37.1	48.8

A Py-GC/MS total ion chromatogram for AS1 is shown in Figure 3. The volatile products consist mainly of alkanes (C_8 to C_{35}), 1-alkene (C_5 to C_{35}), alkylbenzenes (alkyl: C_1 to C_5), alkylnaphthalenes (alkyl: C_1 to C_3) and sulfur compounds (alkyl substituted thiophene, benzothiophene, dibenzothiophene and naphthothiophene). A small amount of isoalkanes and cycloalkanes (alkyl C_5 and C_6 ring) was also identified in the volatile products. Although the asphaltene subfractions AS1 to 6 gave different yields of volatile products, their composition appeared to be similar.

CONCLUSIONS

Asphaltenes derived from petroleum vacuum residua can be further separated into several subfractions based on their solubility in binary mixtures of n-pentane and toluene with different composition. Each subfraction still contains a large number of individual compounds. Distinct differences were observed between subfractions in average molecular weights, molecular weight distribution, aromaticity, and distribution of aliphatic hydrogen.

ACKNOWLEDGMENTS

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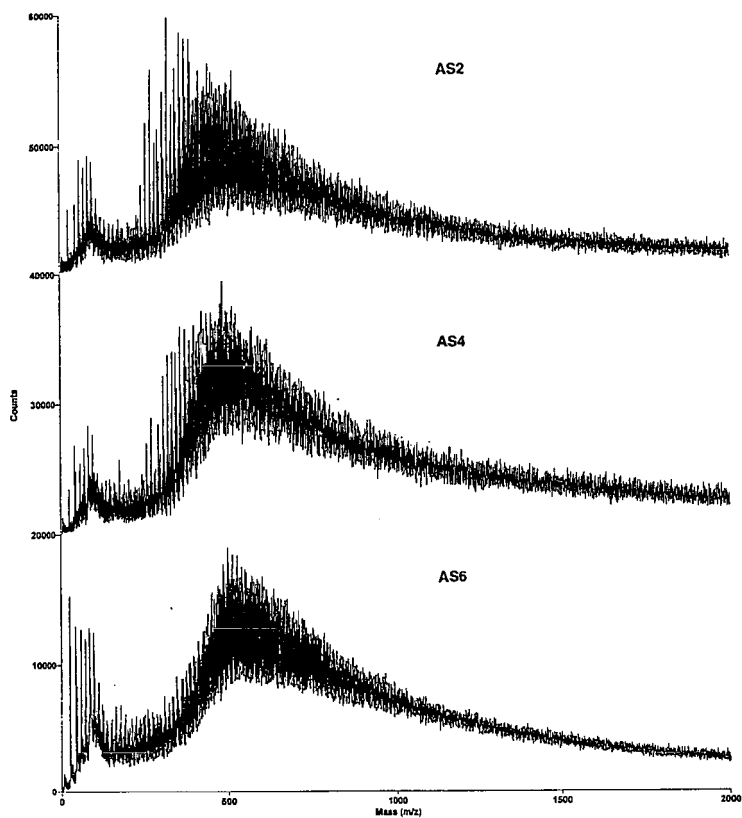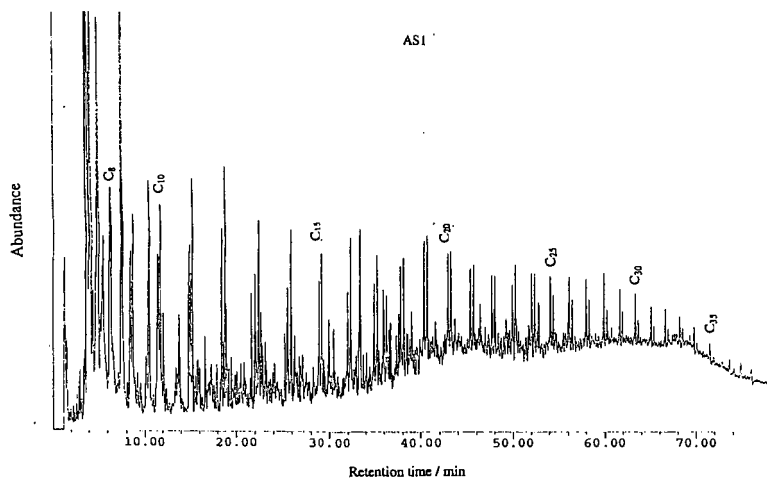Figure 2. LDIMS spectra of three asphaltene subfractions.

Figure 3. Py-GC/MS total ion chromatogram for asphaltene subfraction AS1.